Supporting information for

Ultrafast Delocalization of Cationic States in Poly(N-vinylcarbazole) Solid Leading to Carrier Photogeneration

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CONTENTS

1. Steady-state absorption of the CT complex.

Figure S1 shows the steady-state absorption spectrum of PVCz-CA between 380 and 1000 nm. The broad band with a maximum at 580 nm can be assigned to the charge transfer (CT) transition between the CA and Cz moieties, because the Cz or CA moieties have no sizeable absorption bands in this spectral region. The Cz unit only has absorption bands below 365 nm and CA has a very weak absorption band (n-π^* transition) around 400 nm.

As mentioned in the main text, irradiation at 590 nm corresponds to the direct excitation of the CT band. We also performed experiments with an excitation at 470 nm (see below) which also corresponds to the excitation of the CT band but has a larger excess energy.

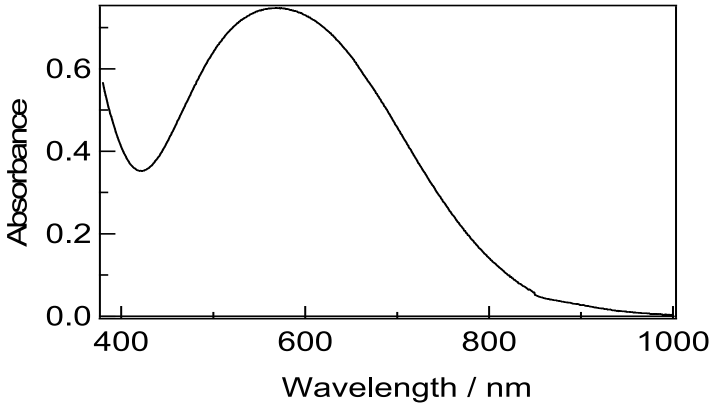


Figure S1 Steady-state absorption spectrum of CA (3 mol % to Cz units) in a PVCz amorphous solid film.

2. Excitation wavelength effect of the temporal evolution of the transient dichroism signals.

The anisotropy measurements with excitations at 470 and 590 nm, monitored at 425 or 460 nm for CA^{-} and 730 or 800 nm for Cz^{+}, are plotted in Figure S2 (differences of monitoring wavelength are due to different setups of the apparatuses). The absolute value of the anisotropy of CA anion monitored at 420 nm is different from that measured at 460 nm because of slight differences in the transition moment of the CA anion band. It however appears that the time profiles are almost independent of the excitation wavelength, indicating that the present time profiles indeed result from the essentially instantaneous preparation of the charge-separated state and its subsequent processes (no appreciable contribution of simple vibrational relaxation or relaxation from the Franck-Condon state to the equilibrium state of the excited CT complex).

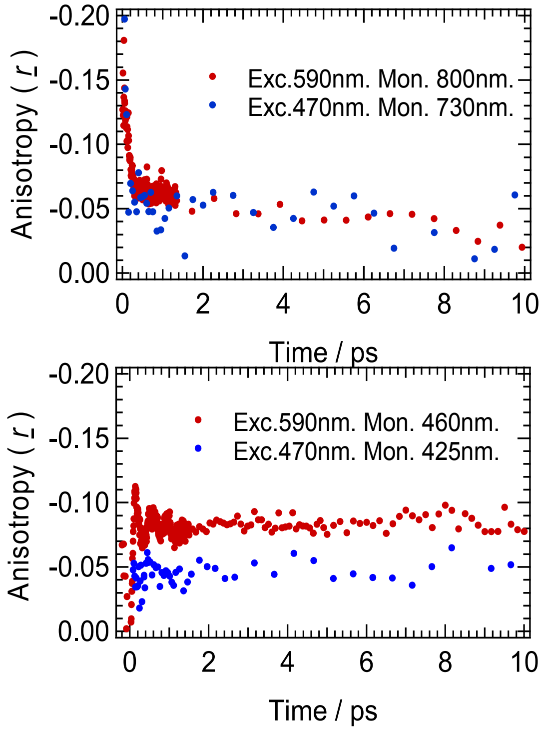
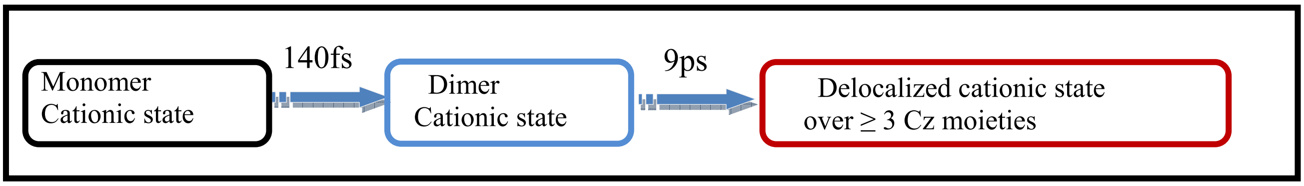


Figure S2. Time profiles of transient dichroism for PVCz-CA solid film after excitation at 470 nm (blue) and 590 nm (red). Monitor wavelength was chosen at 425 or 460 nm for CA^{-} and 730 or 800 nm for Cz^{+}

3. Global and target analysis[S1] of charge resonance band in the near-infrared region.

After excitation of the charge transfer band of the PVCz - CA film, the charge resonance (CR) band due to the delocalized cationic state of the carbazolyl moiety (Cz^+) interacting with one neutral Cz group appears in the NIR region with *ca.* 140-fs time constant. The temporal evolution of the CR band reflects the structural relaxation that leads to the increase of the interaction[S2-S3] and of the hole delocalization.[S4-S5] Let us recall that the anisotropy value of the carbazolyl cation decreases to one half of its initial value with a 140-fs time constant and to less than one third with a 9.0-ps time constant. Figure S3 shows time profiles of the CR band probed at 1600 nm in a rather large time window. The temporal evolution of the CR band is both due to charge recombination and spectral evolution. The blue solid line in Figure S3 is the curve calculated according to the sequential hopping (SH) model,[S6] which is based on sequential hole migration and charge recombination at the initial position of the charge separation. This SH model analysis reproduced quite well the time profile of the transient absorption in the visible region for the charge-separated state in PVCz-CA film [S6-S7]. Hence, the large initial decay at 1600 nm, seen during the first 20 ps could be due to the spectral evolution of the CR band. The red solid line in Figure S3 is the curve calculated with two exponential-functions (the fast rise of the CR band in 140 fs and its spectral evolution in 9 ps), in addition to the SH model.



Scheme S1

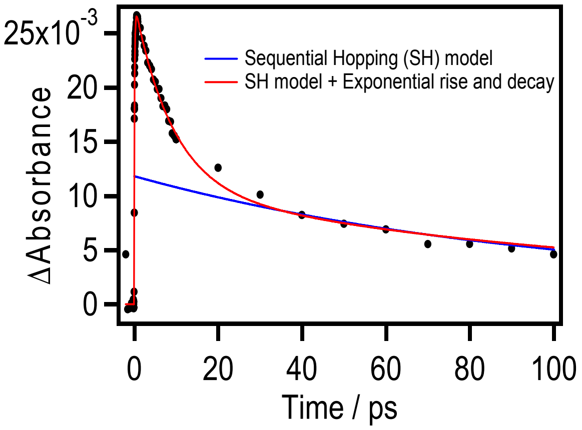


Figure S3. Time profiles of the transient absorbance of PVCz -CA (3 mol %) solid film, monitored at 1600 nm (black circles) after the excitation with a 590nm laser pulse.

In order to precisely elucidate the spectral evolution of the CR band, we applied global and target analysis[S1] to the NIR time-resolved absorption data. With the time function described above, global analysis was performed on 90 time-gated spectra and at 100 wavelengths with the Igor software. From the global analysis data and the kinetic model of Scheme S1, Species-Associated Spectra[S1] (SAS; see Figure S4) were calculated. The species which rises in 140 fs and decays in 9 ps is shown in blue in Figure S4a and the species appearing with the time constant of 9 ps is shown in red. These SAS are quite similar to the spectrum of dimer cation[S4] of Cz (green line) and that of the cationic state[S5] delocalized over more than three Cz units (black line). Figure S4b shows the transient absorption spectra reconstructed from the target analysis at 200 fs, 5 ps and 20 ps. They reproduce quite well the experimental data shown in Figure S4c.

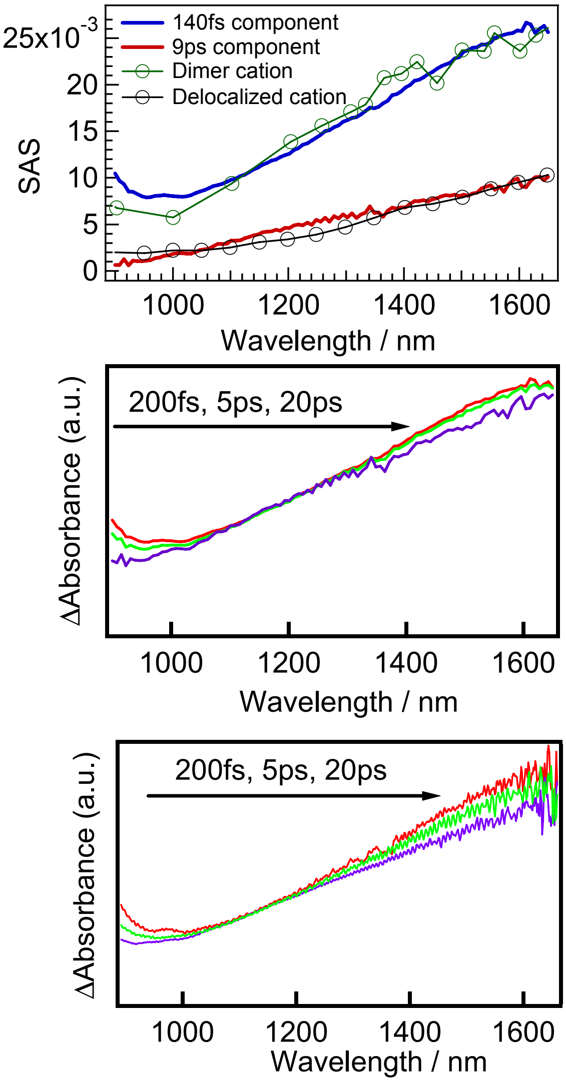


Figure S4. (a) Species-Associated-Spectra (SAS). The species which rises in 140 fs and decays in 9 ps is shown in blue and the species appearing in 9 ps is shown in red. (b) Transient absorption spectra reconstructed from the SAS. (c) Experimental spectra.

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Supporting References

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